

Metal–Organic Polyhedra

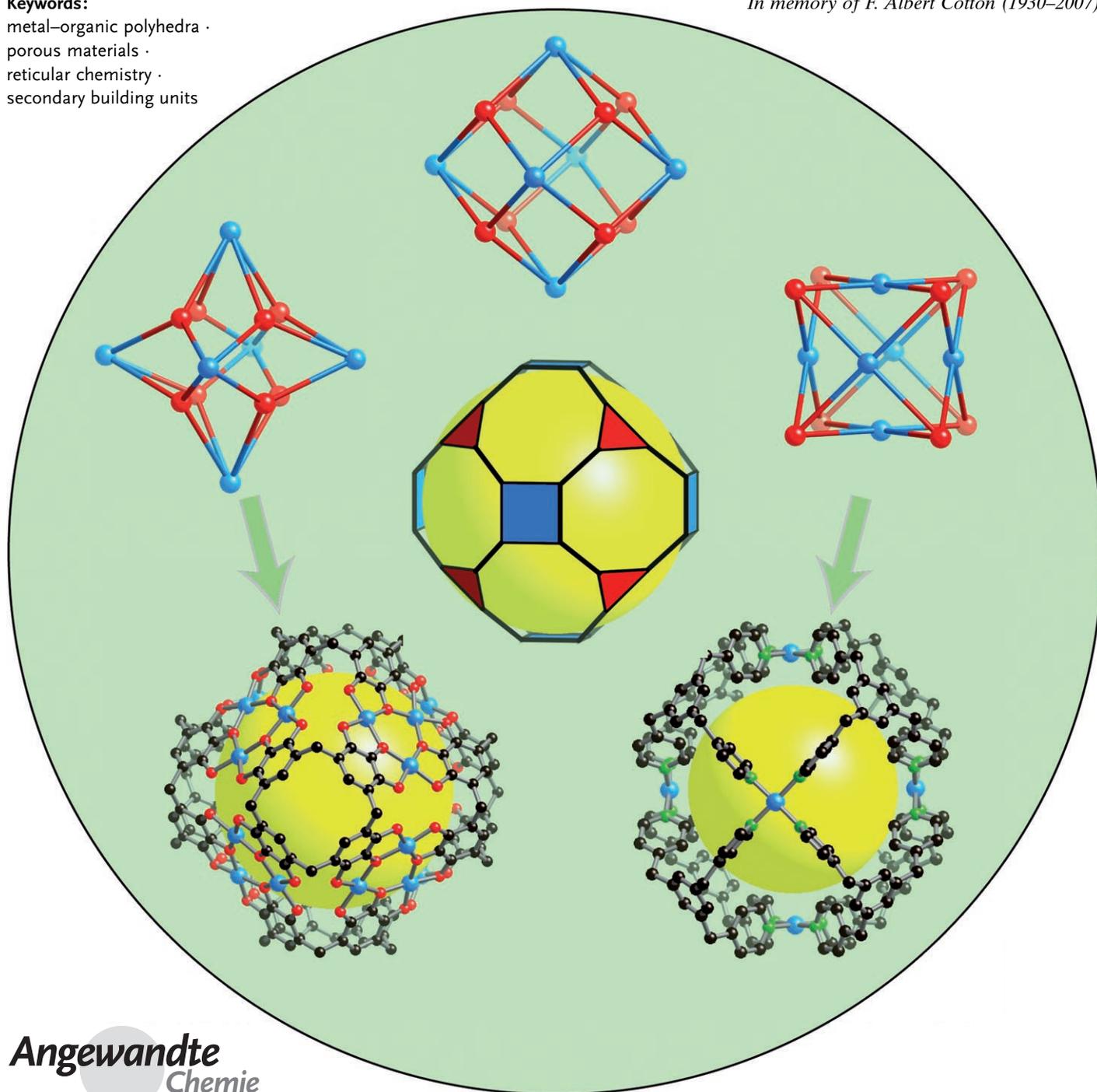
Reticular Chemistry of Metal–Organic Polyhedra

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porous materials ·
reticular chemistry ·
secondary building units

In memory of F. Albert Cotton (1930–2007)



Metal–organic polyhedra (MOPs), are discrete metal–organic molecular assemblies. They are useful as host molecules that can provide tailorable internal volume in terms of metrics, functionality, and active metal sites. As a result, these materials are potentially useful for a variety of applications, such as highly selective guest inclusion and gas storage, and as nanoscale reaction vessels. This review identifies the nine most important polyhedra, and describes the design principles for the five polyhedra most likely to result from the assembly of secondary building units, and provides examples of these shapes that are known as metal–organic crystals.

1. Introduction

Reticular chemistry^[1] is concerned with the design and synthesis of compounds formed from finite secondary building units (SBUs) joined by strong chemical bonds. A basic premise, amply supported by experimental data,^[2] is that when symmetrical SBUs are joined by simple linkers (“struts”) only one of a small number of known, high-symmetry, structures will be formed.^[3,4] A valuable aspect of this approach is that knowing what structures to expect can facilitate unambiguous determination of the structure of complex crystals for which only limited powder X-ray diffraction data are available.^[5] In the most highly developed part of this discipline, that of metal–organic frameworks (MOFs), there are usually two components: a metal-containing, formally cationic, part and an organic, formally anionic, part that combine to produce an often neutral framework. The ability to synthesize predetermined MOF structures allows unprecedented freedom to design porous materials for specific purposes.^[6]

In structures with ditopic organic linkers there will generally be just one kind of inorganic SBU and one kind of link. The nets describing the underlying topology of these structures have just one kind of vertex and one kind of edge—in the jargon they are vertex- and edge-transitive. They have been categorized as *regular*, *quasiregular*, and *semiregular*. We know of just 20 of such nets which have the property that they have embeddings in which there is no inter-vertex distance shorter than the edge length.^[7]

More generally there will be polytopic organic and inorganic SBUs and now the important (*default*) nets will have two kinds of vertex and one kind of edge. Edges of course link unlike vertices, and we have found that with the restriction that there is an embedding in which no distance between unlike vertices is shorter than an edge length, there are 34 of these.^[8] They include the nets of most relevance to reticular chemistry.

Instead of frameworks, one can synthesize what we have termed metal–organic polyhedra (MOPs), the main subject of this review.^[9] Now the SBUs will be topological polygons (we give numerous examples below) and we ask for the ways of linking polygons by one kind of link to form closed structures (“polyhedra”). We will describe the nine such basic structures below. We will then illustrate the principles of their realization in molecules with a number of selected examples. This

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work is not intended to replace the several excellent recent reviews of polyhedral molecules, particularly by pioneers in the field.^[10] Rather it is intended to provide and illustrate a firm conceptual basis for the design and synthesis of such materials.

2. Edge-Transitive Polyhedra

We remark first that it has been known since antiquity that the vertex-transitive polyhedra comprise the five regular (Platonic) solids, which are also edge- and face-transitive, and the Archimedean solids. Of the latter there are two (the quasiregular polyhedra) that are also edge-transitive, but

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which have two kinds of face. The duals^[11] of the regular polyhedra are necessarily regular polyhedra. The duals of the two quasiregular polyhedra are edge- and face-transitive but have two kinds of vertex. It is easy to see that this enumeration is complete.^[12,13]

In Figure 1 we illustrate these nine polyhedra. They include the familiar regular solids (first row in the figure) and the quasiregular polyhedra, the cuboctahedron and icosidodecahedron. The duals of these last two have two kinds of vertex, but one kind of face and are examples of Catalan polyhedra. The polyhedra often have cumbersome names and we find it convenient to refer to them by their three-letter RCSR symbols such as **ido** for icosidodecahedron.^[14] The polyhedra with symbols **ico**, **dod**, **ido**, and **trc** have icosahedral symmetry; the remaining five are cubic.

Also shown in Figure 1 are the polyhedra obtained by replacing the original vertices by a polygon with the number of sides equal to the valence of those vertices. This process of generating related polyhedra is usually referred to as *truncation*, as the new polyhedra can be considered derived from the original ones by slicing off the original vertices, but as we want to extend the process to infinite nets, we prefer the term *augmentation*.^[3] If the original structure has symbol **xyz**, we often write the symbol of the augmented version as **xyz-a**. These nine augmented polyhedra represent the nine ways of linking polygons with one kind of link to form closed shapes and are the focus of this review.^[15] As may be seen from Figure 1 the polygons may have three, four, or five vertices and will be realized by SBUs that have three, four, or five *points of extension* (linking sites).

The polyhedral molecule may be either composed of one kind of SBU linked by a ditopic linker, or of two SBUs with more than two points of extension. An SBU with *n* points of

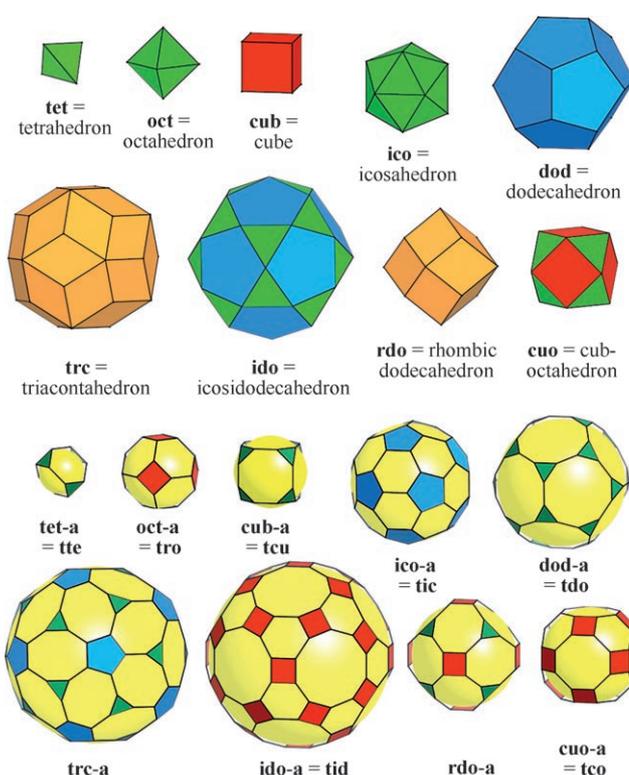
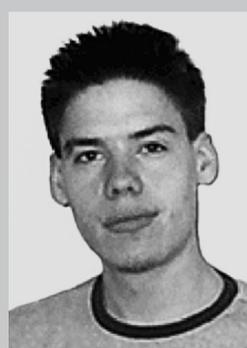


Figure 1. Top two rows: the nine edge-transitive convex polyhedra. Bottom: their corresponding augmented derivatives. The symbols are the RCSR symbols.^[14]

extension is referred to as *n*-valent. In the following sections we will focus particularly on the cases with cubic symmetry as there are few, if any, icosahedral molecules that are built up



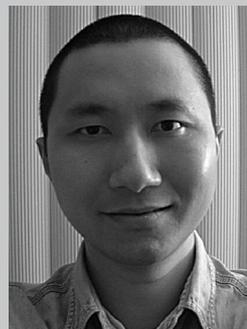
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from SBUs and for which there are atomic coordinates. The case of the cube is special (it is the only regular polyhedron with even-sided faces). With one kind of link it can correspond either to eight identical SBUs linked by a ditopic linker, or to four SBUs of one kind (say cationic) linked to four SBUs of a different kind (anionic). In the latter case we call it a *heterocube*.

3. SBUs and linkers

There are two important angles that characterize the geometry of an assembly. The first is the angle η between the links from the SBU (Figure 2). The second is the angle θ between the links of a ditopic linker (Figure 3). We give some examples of special cases because the first task of the designer and would-be synthesizer is to design SBUs and linkers of the correct geometry for the required product.

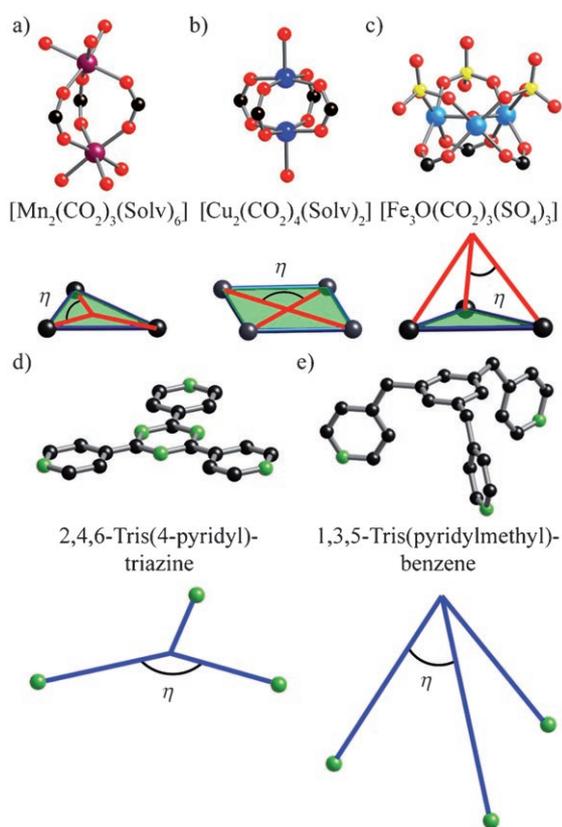


Figure 2. Examples of SBUs: a) Two Mn centers (pink) bridged by three carboxylates (C black, O red), with terminal solvent ligands on each Mn center (red spheres); b) two Cu centers (blue) bridged by four carboxylates, with a terminal solvent ligand on each Cu center; c) three Fe centers (light blue) bridged by three carboxylates, with capping sulfate groups (S yellow). Below (a) through (c) are the corresponding polygons highlighting the angle η between the coordination vectors of the links. The green polygons are constructed between the points of extension of the inorganic cluster. d, e) Examples of organic SBUs (C black, N green) and the corresponding coordination vectors.

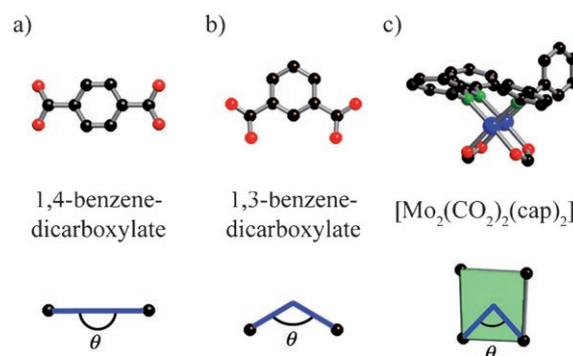


Figure 3. Examples of linkers with angle θ between links. Linkers can be organic, as in (a) and (b), or inorganic, such as the capped Mo cluster in (c), in which the shape of the cluster, including two bulky amidinate capping (cap) ligands, is described by the green square. The color scheme is the same as in Figure 2 (Mo = blue).

4. Molecules Based on the Tetrahedron

Here we have four trivalent SBUs with links at an angle η joined by ditopic linkers bent at an angle θ . Two extreme cases, $\eta = 60^\circ$, $\theta = 180^\circ$ and $\eta = 120^\circ$, $\theta = 70.5^\circ$ are shown in Figure 4. An intermediate case $\eta = \theta = 109.5^\circ$ corresponds to the vertices of an adamantane cage. In general if we set $x = \sin(\eta/2)$ and $y = \sin(\theta/2)$, $4x^2 - 4xy + 3y^2 = 2$.

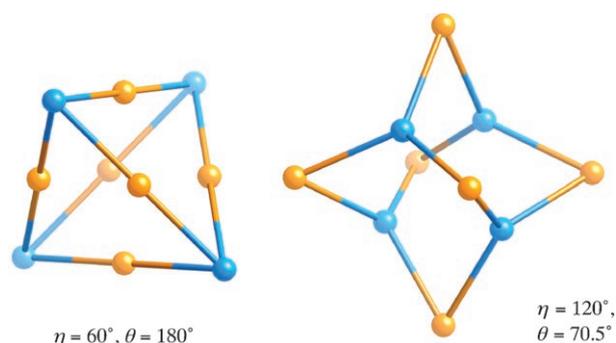


Figure 4. Two configurations of four trivalent SBUs linked to form a tetrahedron.

The first extreme case is represented by IRMOP-51 (Figure 5),^[16] which is composed of sulfate-capped basic iron carboxylate trimer cluster SBUs connected by biphenyl linkers. The iron carboxylate cluster has three of its six points of extension capped by sulfate ligands, leaving three points of extension with $\eta = 68.7^\circ$, and the biphenyl linker is almost linear ($\theta = 175.9^\circ$). IRMOP-50, -52, and -53 share the same geometry, with different linear linkers: benzene, tetrahydropyrene, and terphenyl, respectively, instead of biphenyl.^[16]

The second extreme case is illustrated in Figure 6.^[17] In this case, we consider η as the average of the angles between points of extension for the T-shaped, mono-capped Mo paddle-wheel (two of 90° , one of 180°), so $\eta = 120^\circ$. In addition, we consider θ as the average of the six thiophene-3,4-dicarboxylate linkers (four linkers of 73.1° and two of

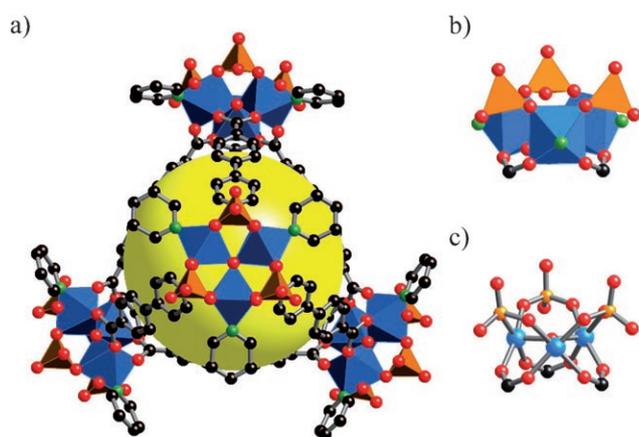


Figure 5. An example of a tetrahedron in the first extreme case. a) The tetrahedral structure of IRMOP-51; b) the $[\text{Fe}_3\text{O}(\text{CO}_2)_3(\text{SO}_4)_3]^{2-}$ triangular SBU with angle η close to 60° , shown in polyhedral form, in which the bridging sulfate ions serve as the capping ligands and the carboxylate carbon atoms are the points of extension; c) the corresponding ball-and-stick version. (Fe blue, S orange, O red, C black, N green). The yellow sphere in (a) delineates the empty space at the center of the molecule. The coordinating pyridine solvent molecules are omitted in (b) and (c) for clarity.

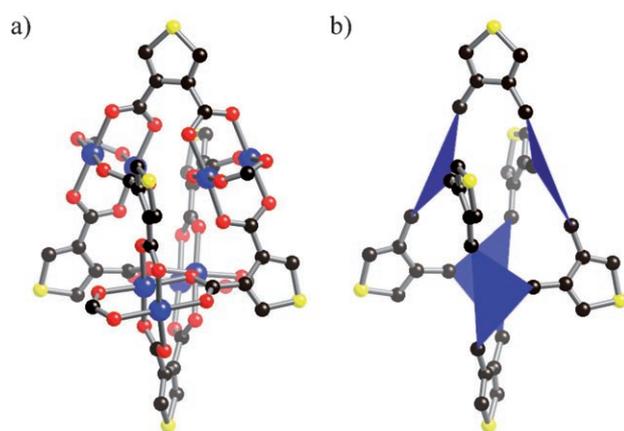


Figure 6. An example of a tetrahedron close to the second extreme case. a) The tetrahedron is composed of four Mo paddle-wheel clusters and six 3,4-thiophenedicarboxylate linkers. One bridging site of each Mo paddle-wheel is occupied by a $t\text{Bu-CO}_2^-$ ligand. b) The capped paddle-wheel SBUs are represented by blue triangles, showing their tritopic nature. (The $t\text{Bu}$ groups are omitted for clarity; Mo blue, C black, O red, S yellow).

65.7°), thus $\theta = 70.6^\circ$. This molecule exhibits a large deviation from ideality, accommodated in the assembly by distorting the underlying tetrahedral shape and lowering the point group symmetry from T_d to D_2 . An essential element of this distortion is the twisting of carboxylate groups out of the thiophene plane (the torsion angles are: 56.0° and 1.2° for one type of linker; 33.4° and 33.4° for the other), as shown in Figure 6.

Another example of tetrahedral construction of the second extreme case, with organic SBUs and inorganic linkers, is composed of 1,3,5-benzenetricarboxylate (btc) SBUs linked by capped Mo paddle-wheel squares (Figure 7,

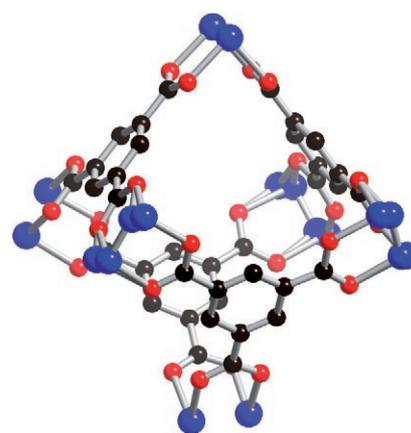


Figure 7. The tetrahedral cage formed by btc SBUs ($\eta = 120^\circ$) linked by capped Mo paddle-wheels ($\theta = 83.4^\circ$). (Mo blue, C black, O red; capping groups are omitted for clarity).

$\eta = 120^\circ$, $\theta = 83.4^\circ$).^[18] The rigidity of btc limits any adjustments to η ; instead, angular tuning to form the structure comes from the non-ideal coordination of the carboxylate groups to the capped Mo dimer cluster.

A third tetrahedral compound close to the second extreme case, again with organic SBUs and inorganic linkers is shown in Figure 8 ($\eta = 118.7^\circ$ and 120° , $\theta = 84.8^\circ$ and

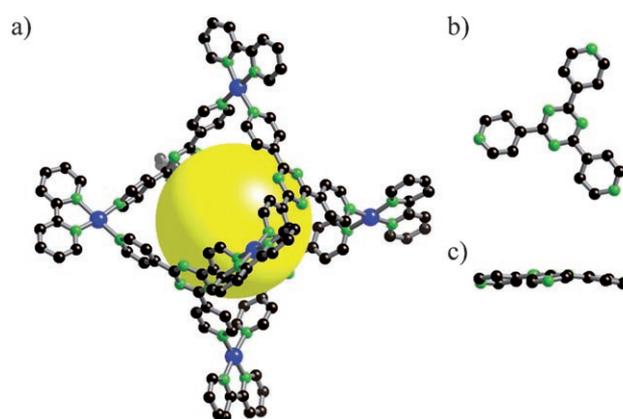


Figure 8. a) The tetrahedral cage $[(\text{bpy})_6\text{Pd}_6(\text{tpt})_4]^{12+}$ ($\text{bpy} = 2,2'$ -bipyridine, $\text{tpt} = 2,4,6$ -tris(4-pyridyl)-triazine); b) the top view and c) the side view of one tpt SBU observed in the tetrahedral assembly. (Pd blue, C black, N green).

86.2°).^[19] The 2,2'-bipyridine-capped Pd linker has an angle θ slightly less than 90° , a significant deviation from 70.5° . The large 2,4,6-tris(4-pyridyl)triazine (tpt) SBU is capable of bending its shape slightly to afford the required η (Figure 8b and c). Fujita and co-workers reported a variety of applications for this and similar tetrahedral compounds, made from Pd^{2+} or Pt^{2+} , tpt, and various capping ligands, often depicting them as octahedral molecules missing alternate faces.^[20–25]

Figure 9 shows an ideal example of the intermediate case, $\eta = \theta = 109.5^\circ$, that has a structure derived from NMR evidence.^[26] Four tri-topic organic SBUs are connected by six organoplatinum linkers. The centers of both the metal

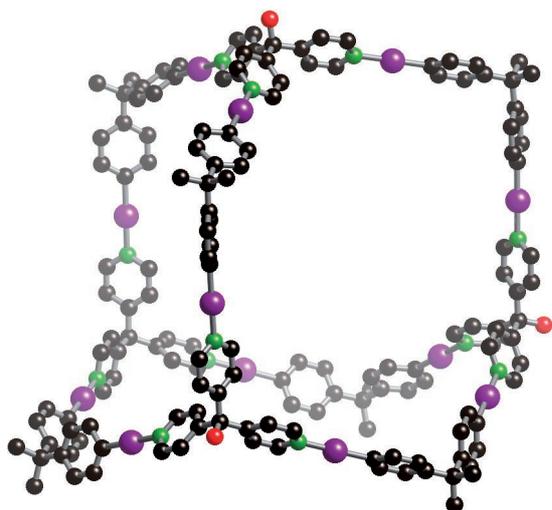


Figure 9. The proposed structure of a molecule of the special situation $\eta = \theta = 109.5^\circ$ of a tetrahedron; the structure was proposed on the basis of NMR evidence. The organic SBUs, with sp^3 -hybridized C centers, are linked to the organoplatinum links, which also have sp^3 -hybridized C centers. Two phosphine ligands on each Pt center are omitted for clarity. (Pt purple, C black, N green, OH red).

linker and organic SBU are sp^3 -hybridized C atoms which are expected to impart angles close or equal to 109.5° .

5. Molecules Based on the Octahedron

Here we have six tetravalent SBUs with links at an angle η joined by ditopic linkers bent at an angle θ . Two extreme cases, $\eta = 60^\circ$, $\theta = 180^\circ$ and $\eta = 90^\circ$, $\theta = 90.0^\circ$ are shown in Figure 10. In general if we set $x = \sin(\eta/2)$ and $y = \sin(\theta/2)$, $4x^2 - 4xy + 2y^2 = 1$.

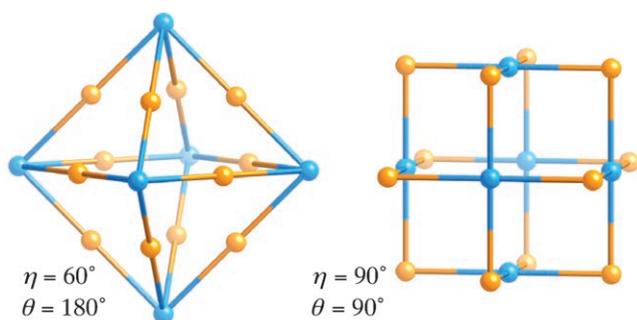


Figure 10. Two configurations of six tetravalent SBUs linked to form an octahedron.

We first note the lack of an example for the first extreme situation, probably due to the scarcity of tetravalent metal SBUs with an angle $\eta = 60^\circ$.

The first example of the second extreme situation ($\eta = 90^\circ$, $\theta = 90.0^\circ$) is MOP-28 (Figure 11).^[27] The Cu paddle-wheel is slightly distorted but maintains an average angle η of 90.0° . The paddle-wheel is connected by 2,2':5',2''-terthio-

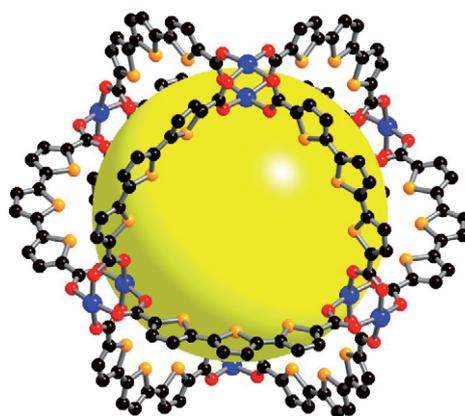


Figure 11. MOP-28, an example of the construction of an octahedron of the second extreme case. Cu paddle-wheel SBUs ($\eta = 90.0^\circ$) are connected by ttdc linkers ($\theta = 90^\circ$). (Cu blue, C black, O red, S orange).

phene-5,5''-dicarboxylate (ttdc) links, which have an angle θ of 90.0° .

Another example comparable to the second extreme situation is shown in Figure 12 for which the actual angles are

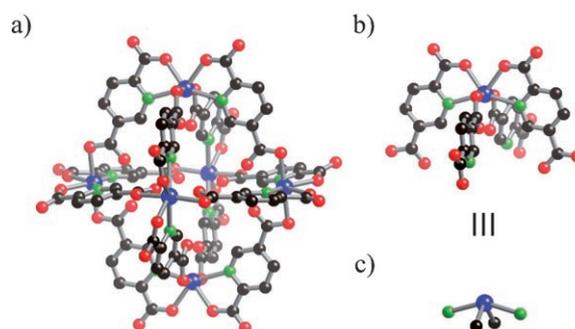


Figure 12. An example of the construction of an octahedron of the second extreme case. a) The octahedral assembly $[In_6(2,5-pdc)_{12}]^{6-}$ (2,5-pdc = 2,5-pyridinedicarboxylate); b) The geometry of a single In^{3+} SBU defined by using the carbon atom of the carboxylate group at the 5-position and the nitrogen atom of each linker as the points of extension, shown simplified in (c). (In blue, C black, N green, O red).

$\eta = 82.2^\circ$, $\theta = 120^\circ$.^[28] The points of extension are the C atom of the carboxylate group at the 5-position and the N atom of the 2,5-pyridinedicarboxylate linker (the carboxylate at the 2-position is irrelevant for topological analysis). Therefore, the linker has an angle $\theta = 120^\circ$ and the geometry of the metal SBU deviates from square planar, $\eta = 90^\circ$. When $\theta = 120^\circ$, the general relation between η and θ for this construction type gives $\eta = 86.2^\circ$. The calculation shows that a large deviation in θ of the ditopic linker ($120^\circ - 90^\circ = 30^\circ$) can be accommodated by a small deviation in η of the square metal SBU ($90^\circ - 86.2^\circ = 3.8^\circ$). The capability of the relatively flexible single metal ion vertex to tune η is the key to this construction.

6. Molecules Based on the Cube

Here we have eight trivalent SBUs with links at an angle η joined by ditopic linkers bent at an angle θ . Two extreme cases, $\eta = 90^\circ$, $\theta = 180^\circ$ and $\eta = 120^\circ$, $\theta = 109.5^\circ$ are shown in Figure 13. In general if we set $x = \sin(\eta/2)$ and $y = \sin(\theta/2)$, $4x^2 - 4\sqrt{2}xy + 3y^2 = 1$.

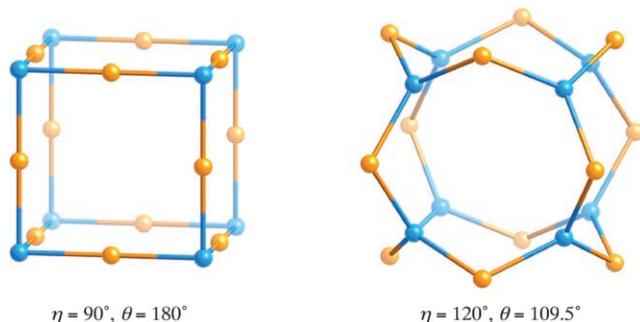


Figure 13. Two configurations of eight trivalent SBUs linked to form a cube.

Figure 14 illustrates an example of the first situation with a structure based on NMR evidence.^[29] The capped Ru SBUs have angle $\eta = 90^\circ$ imparted by the octahedral coordination environment. The SBUs are connected through linear 4,4'-bipyridine linkers ($\theta = 180^\circ$).

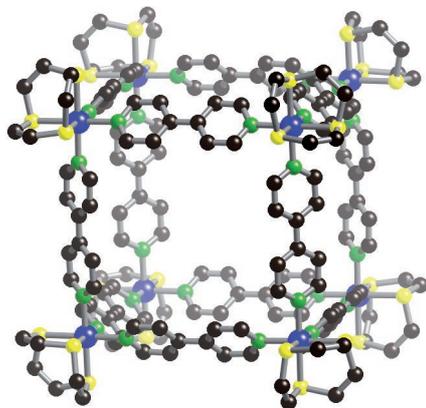


Figure 14. An example of the construction of a cube. The model of the simple cubic structure $[L_3Ru_8(bpy)_{12}]^{16+}$ ($L = 1,4,7$ -trithionane; $bpy = 4,4'$ -bipyridine) proposed based on NMR evidence. (Ru blue, C black, N green, S yellow).

Another example of the first extreme case is shown in Figure 15 ($\eta = 96.0^\circ$, $\theta = 176.2^\circ$).^[30] The points of extension are the N atoms of the 4,5-imidazoledicarboxylate linkers (Figure 15 a and b, in green). The chelation of this linker to Ni^{2+} centers has rendered Ni-Im-Ni almost linear, giving rise to an angle θ close to 180° (Figure 15 b, in green).

Significantly, this example can be viewed in comparison with the second extreme case ($\eta = 120^\circ$, $\theta = 109.5^\circ$), if one uses the centroids of the chelating units as points of extension

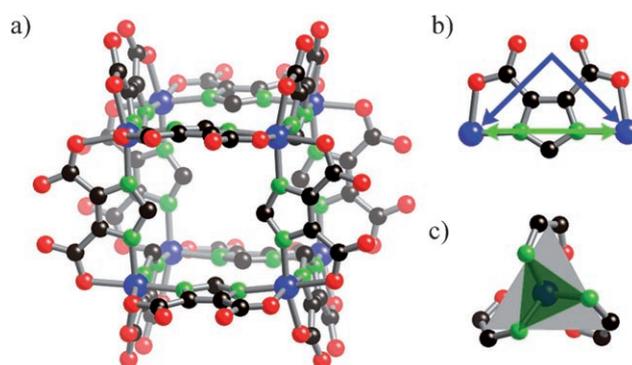


Figure 15. An example of the construction of a cube. a) The cubic cage composed of eight Ni^{2+} centers and twelve 4,5-imidazoledicarboxylate linkers. b) The 4,5-imidazoledicarboxylate linker whose coordination vectors depend on the choice of points of extension: green arrows using the N atoms; blue arrows using the centroids of C–C bonds of the $NCCO^-$ chelating units. c) The $[Ni(NCCO)_3]^-$ SBU whose shape depends on the choice of points of extension: green triangle using the N atoms; gray triangle using the centroids of C–C bonds of the $NCCO^-$ chelating units. (Ni blue, C black, N green, O red).

instead of the N atoms on the imidazole ring. Consequently the metal SBUs are now planar triangles with $\eta = 120^\circ$ and the angle θ of the linker is 92.3° (Figure 15 b and c, blue vectors and grey triangle, respectively). The observed θ shows a large deviation from the expected 109.5° . This is because the points of extension do not orient toward the edge-centers, as assumed in deriving the general relation between η and θ for this construction type. The N atoms of the linker orient toward the edge-centers of the Ni_8 cube and they define the ideal orientation (Figure 15 c, green triangle). A rotation of the triangle defined by the centroids of the chelating units (Figure 15 c, gray triangle) from the ideal orientation by 23° is responsible for the observed large discrepancy in θ ($109.5^\circ - 92.3^\circ = 17.2^\circ$).

7. Molecules Based on the Cuboctahedron

Here we have twelve tetravalent SBUs joined by ditopic linkers. Two extreme cases are shown in Figure 16. Notice that, as the tetravalent SBUs are not at sites of fourfold symmetry, there are no longer simple expressions relating the

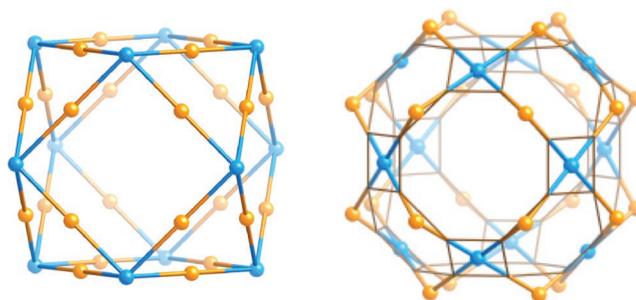


Figure 16. Two configurations of twelve tetravalent SBUs linked to form a cuboctahedron. The thin dark lines in the sketch on the right outline a truncated (augmented) cuboctahedron.

angles. If there are straight linkers and the SBU centers are at the vertices of a cuboctahedron (Figure 16, right), then there are two angles (60° and 90°) between the links from the center of the SBU. If the SBU is square with 90° between links (Figure 16, right) then the ditopic linker must be bent at an angle of 117° (it is important that this is close to 120°).

Figure 17a shows the structure of MOP-1, an example of this construction type composed of a Cu paddle-wheel SBU ($\eta = 90^\circ$) and a 1,3-benzenedicarboxylate linker ($\theta = 120^\circ$).^[9] Another good example is shown in Figure 17b; in this

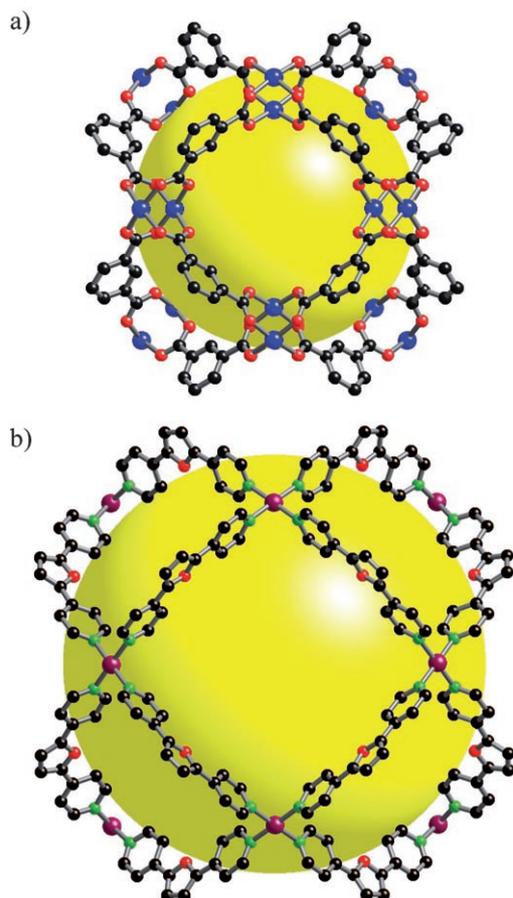


Figure 17. Two examples of the construction of a cuboctahedron using square planar metal SBUs. a) MOP-1 composed of 12 Cu paddle-wheel SBUs and 24 1,3-benzenedicarboxylate linkers; b) an even larger cuboctahedral cage composed of 12 Pd^{2+} centers and 24 2,5-bis(4-pyridyl)furan linkers. (Cu blue, Pd magenta, C black, O red, N green).

structure Pd^{2+} centers are linked by 2,5-bis(4-pyridyl)furan linkers ($\eta = 90^\circ$, $\theta = 122.8^\circ$) to afford the cuboctahedral assembly.^[31]

Fujita and co-workers have reported similar examples of cuboctahedra, including examples with pyridyl groups meta to each other on benzene rings ($\theta = 120^\circ$) and with pendant groups directed either into or out of the cage, sometimes referred to as a “sphere.”^[32–34]

8. Molecules Based on the Heterocube

Here we have two trivalent SBUs with links at an angle η_1 and η_2 . We assume that they are joined together so that the links from two joined SBUs are colinear. Two extreme cases, $\eta_1 = \eta_2 = 90^\circ$, and $\eta_1 = 120^\circ$, $\eta_2 = 33.6^\circ$ are shown in Figure 18. In general if we set $x = \sin(\eta_1/2)$ and $y = \sin(\eta_2/2)$, $3x^2 - 4xy + 3y^2 = 2$.

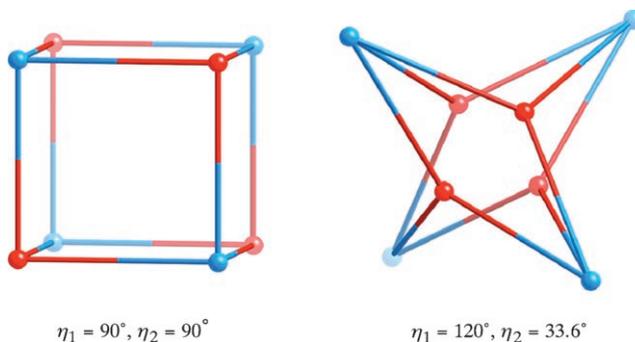


Figure 18. Two configurations of eight trivalent SBUs of two kinds linked to form a heterocube.

The first extreme case of heterocube formation ($\eta_1 = \eta_2 = 90^\circ$) is represented by a metal cyanide cage shown in Figure 19 ($\eta_1 = 93.6^\circ$, $\eta_2 = 91.5^\circ$).^[35] The four $\{\text{Co}(\text{H}_2\text{O})_3(\text{CN})_3\}$ centers are assigned η_1 , whereas the four $\{\text{Co}(\text{tach})(\text{CN})_3\}$ units are assigned η_2 (tach = *cis,cis*-1,3,5-triaminocyclohexane). This assignment is consistent with the synthetic approach and the intrinsic tetrahedral symmetry of this cage. If both types of Co centers are counted as vertices, this structure represents construction of a heterocube.

A good example of the second extreme case ($\eta_1 = 120^\circ$, $\eta_2 = 33.6^\circ$) is shown in Figure 20.^[36] The first of the two SBUs, the trithiocyanurate unit, has η_1 of 120° (Figure 20a). The

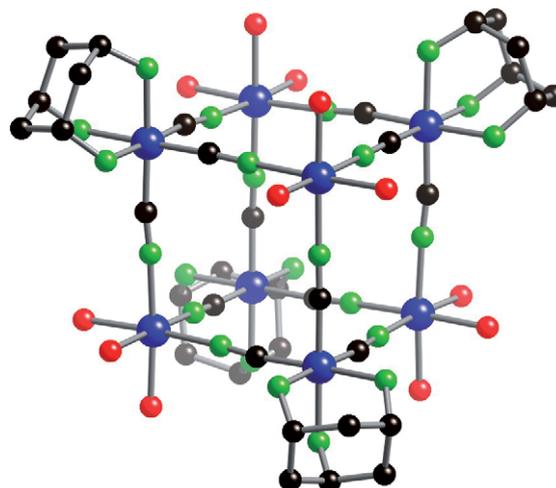


Figure 19. An example of the first extreme case ($\eta_1 = \eta_2 = 90^\circ$) of a heterocube. Four $\{\text{Co}(\text{H}_2\text{O})_3(\text{CN})_3\}$ SBUs have $\eta_1 = 93.6^\circ$, and four $\{\text{Co}(\text{tach})(\text{CN})_3\}$ SBUs have $\eta_2 = 91.5^\circ$. (Co blue, C black, N green, O of H_2O red).

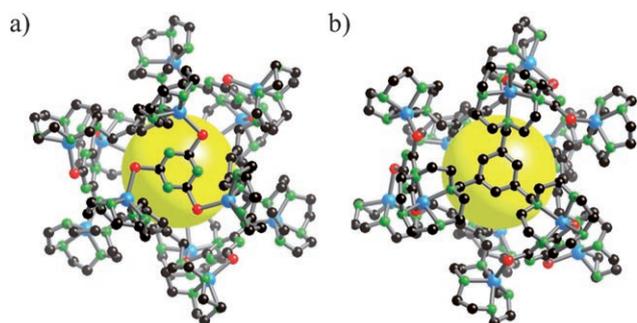


Figure 20. An example of a heterocube with the formula $[(Zn_3L)_4(tca)_4]^{12+}$, $L = 1,3,5$ -tris-(1,4,7,10-tetrazacyclododecan-1-ylmethyl)benzene, $tca =$ trithiocyanurate; a) view of the molecule with the tca SBU in the center; b) view of the molecule focusing on the Zn_3L SBU; (Zn blue, C black, N green, S red).

second SBU, with η_2 of 35.6° , is composed of the Zn_3L unit ($L = 1,3,5$ -tris-(1,4,7,10-tetrazacyclododecan-1-ylmethyl)benzene) (Figure 20b), connected to the first SBU by Zn–S bonds. The Zn equatorial coordination sites are all occupied by the macrocycle ligand of the second SBU, leaving only the apical positions open for the S atoms of the trithiocyanurate SBU to coordinate.

MOP-54 is an example of the second extreme case wherein large deviations from the special angles occur ($\eta_1 = 109^\circ, 115^\circ, 116^\circ, \eta_2 = 65.2^\circ, 67.9^\circ, 68.3^\circ$; Figure 21).^[16] Interestingly, the observed η_1 and η_2 of MOP-54 actually fit into the

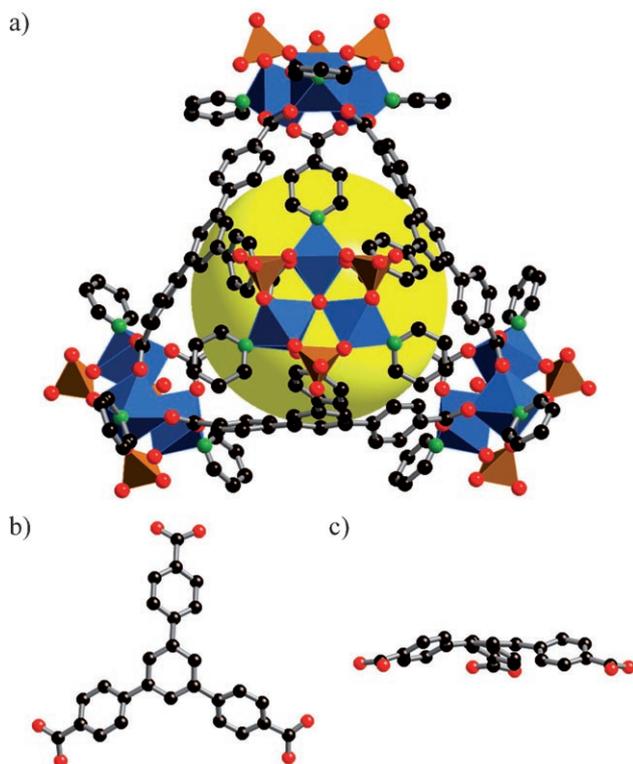


Figure 21. An example of a heterocube molecule. a) The structure of MOP-54; b) the top view and c) the side view of the 1,3,5-benzenetribenzoate (btb) SBU observed in the crystal structure of MOP-54. (Fe blue, S orange, O red, C black, N green).

general equation well. When $\eta_2 = 67.1^\circ$ (the average of the observed values of η_2), the equation gives $\eta_1 = 108.7^\circ$.

The calculation shows that, in the (η_1, η_2) region under investigation, a large difference in η_2 ($67.1^\circ - 33.6^\circ = 33.5^\circ$) can be compensated by a relatively small change in η_1 ($120^\circ - 108.7^\circ = 11.3^\circ$) due to the property of the function itself. The large triangular linker 1,3,5-benzenetribenzoate (btb) distorts to accommodate the required angle η_1 (Figure 21 b and c). The remaining discrepancy in η_1 is addressed by the distorted Fe-carboxylate coordination linkage.

9. Molecules Based on the Rhombic Dodecahedron

Here we have eight trivalent SBUs and six tetraivalent SBUs with links at an angle η_1 and η_2 respectively. We assume that they are joined together so that the links from two joined SBUs are colinear. There are now three extreme cases: a) $\eta_1 = 120^\circ, \eta_2 = 48.2^\circ$, b) $\eta_1 = 109.5^\circ, \eta_2 = 70.5^\circ$, c) $\eta_1 = 60^\circ, \eta_2 = 90^\circ$ (Figure 22). In general if we set $x = \sin(\eta_1/2)$ and $y = \sin(\eta_2/2)$,

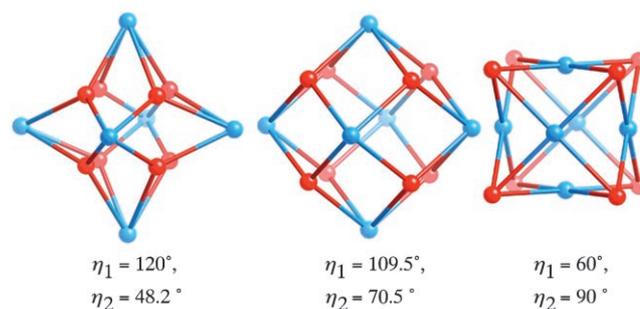


Figure 22. Three configurations of eight trivalent SBUs (red) linked to six tetraivalent SBUs (blue) to form a rhombic dodecahedron.

$2x^2 - 2\sqrt{2}xy + 3y^2 = 1$. In case (b) the vertices are at the positions of the vertices of an ideal rhombic dodecahedron. In case (a) the trivalent vertices are in the faces of an octahedron of the tetraivalent vertices, and this configuration is often referred to, we think wrongly, as an octahedron. In case (c) the tetraivalent vertices are in the faces of a cube of the trivalent vertices, and this configuration is often referred to, again we think wrongly, as a cube.

We are not aware of any reported structure illustrating the special case (b).

Figure 23 shows a MOP structure of extreme situation (a), constructed from pyrogallol[4]arene units coordinated to copper through its oxygen atoms to form Cu_3O_3 triangles.^[37] The large cone-shaped pyrogallol[4]arene SBU has an angle $\eta_2 = 42.2^\circ$, whereas the planar Cu_3O_3 SBU has an angle $\eta_1 = 120^\circ$.

The $[(Me_3tacn)_8Cr_8Ni_6(CN)_{24}]^{12+}$ cage shown in Figure 24 ($\eta_1 = 88.1^\circ, \eta_2 = 89.1^\circ$) is an interesting example to compare with extreme situation (c).^[38] The geometry of the $[Ni(CN)_4]^{2-}$ SBU is very close to square planar ($\eta_2 = 89.1^\circ$), but the angle η_1 of the $(Me_3tacn)Cr(CN)_3$ SBU deviates from the expected value greatly ($88.1^\circ - 60^\circ = 28.1^\circ$). Figure 24 b shows how this structure can form with such large deviation in η_1 . The

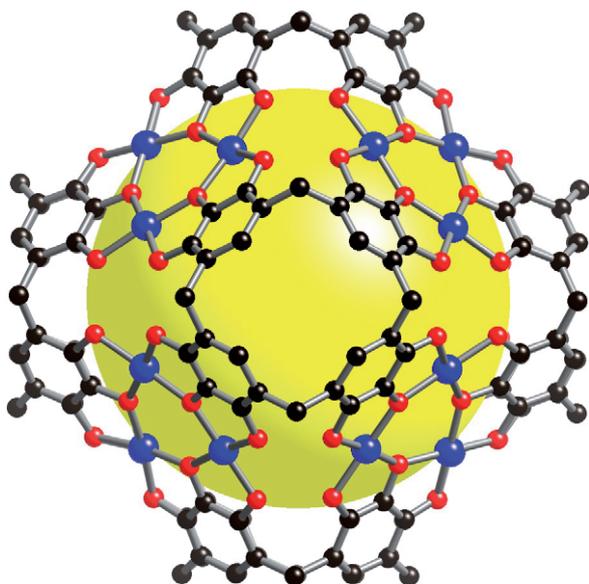


Figure 23. An example of a rhombic dodecahedron of extreme situation (a). The cage is composed of eight trivalent planar Cu_3O_3 SBUs and six tetravalent pyrogallol[4]arene SBUs. (Cu blue, C black, O red).

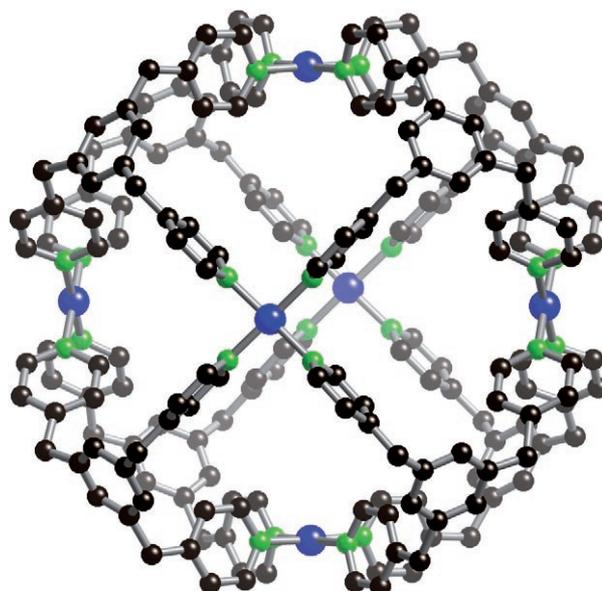


Figure 25. An example a rhombic dodecahedron of extreme situation (c). The cage is composed of six square planar Pd^{2+} centers and eight 1,3,5-tris(4-pyridylmethyl)benzene linkers. (Pd blue, C black, N green).

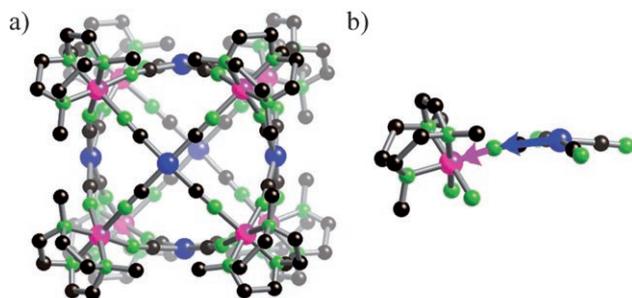


Figure 24. An example of a rhombic dodecahedron of extreme situation (c). a) The cubic cage $[(\text{Me}_3\text{tacn})_3\text{Cr}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$ ($\text{Me}_3\text{tacn} = N,N',N''$ -trimethyl-1,4,7-triazacyclononane); b) One pair of the $(\text{Me}_3\text{tacn})\text{Cr}(\text{CN})_3$ SBU and the $[\text{Ni}(\text{CN})_4]^{2-}$ SBU with the coordination vectors shown as the pink and blue arrows, respectively. (Cr pink, Ni blue, C black, N green).

coordination vectors of the Ni SBU (blue arrow) and the Cr SBU (pink arrow) are not colinear, and have a significant angle between them (the supplement of the bond angle C–N–Cr: $180^\circ - 169.0^\circ = 11.0^\circ$).

Another example of extreme situation (c) is shown in Figure 25 ($\eta_1 = 90^\circ$, $\eta_2 = 55.6^\circ$).^[39] The 1,3,5-tris(4-pyridylmethyl)benzene SBU in this particular conformation is very useful in that it adopts an angle η_1 close to 60° .

10. Summary of Deviations

All of the above examples exhibit some degree of deviation from the angles calculated for extreme situations. The factors contributing to the tolerance for the deviations in MOPs from the special angles can be summarized into two categories according to the applicability of the general relations between the angles η and θ to the structures under

question: small deviations in one angle ($< 10^\circ$) and large deviations in one angle ($> 10^\circ$).

As has been detailed above, small deviations in one of the two angles ($< 10^\circ$) are generally within a tolerance level that the other angle does not need adjustment. Large deviations in one angle are accommodated by small deviations in the other angle; the second angle is always close to what is calculated to be the accommodating angle based on the equation appropriate for the polyhedron, as is seen in three of the four molecules with significant deviation.

The molecule in Figure 8 is an excellent example: the equation shows that for an average θ value of 85.5° , η should be 118.3° , whereas the average η value is 119.4° ; a 1.1° difference. The molecule in Figure 12 is similar: a large deviation in θ from the extreme situation is accommodated by a value of η close to what is calculated from the function relating the two in an octahedral structure, as has been detailed above. This also holds true for MOP-54 in Figure 21, as detailed above. In these cases, one building block distorts slightly to adopt an angle close to that required for polyhedron formation.

There are three special cases, in which the general accommodation scheme discussed above does not hold true. The first is the tetrahedral molecule shown in Figure 6. The SBU in this case has angles η of 90° , 90° , and 180° between points of extension. While the average value for η is 120° , the large disparity in individual values of η leads to a significant distortion of the molecule's structure.

The second special case is that of the cubic molecule in Figure 15. Specifically, the second construction scheme presented shows significant deviation from the extreme angles ($\eta = 120^\circ$, $\theta = 109.5^\circ$). As discussed above, the SBU points of extension, and accordingly the linkers, are not oriented toward the edge-centers of the second extreme cube. The

octahedral coordination of the Ni atoms prevents such orientation.

Finally, the third special case is the rhombic dodecahedron in Figure 24. In this molecule, a significant deviation in η_1 is not accommodated by a change in η_2 . Instead, the Ni–C and Cr–N coordination vectors are not colinear. This permits the necessary flexibility for the formation of the molecule.

11. Summary and Outlook

This review provides a basis for predictable synthesis and subsequent investigation of MOPs. Both the SBUs and the linkers can be synthesized with a predetermined geometry using appropriate reaction conditions and starting materials, and the possibilities are virtually limitless. In particular, we have shown the importance of control of angles of SBUs and linkers, although we have remarked that nature is generally forgiving of small deviations from ideality. These concepts will be of increasing importance as the field of MOP reticular chemistry continues to grow. We have limited our examples, with two exceptions, to those for which explicit coordinates were available for the atoms. We have not found such examples for molecules based on icosahedral polyhedra and the preparation of these remains a nice challenge. However, in this connection, attention should be called to the elegant dodecahedral molecules reported by Olenyuk et al., for which atomic coordinates are not available.^[40]

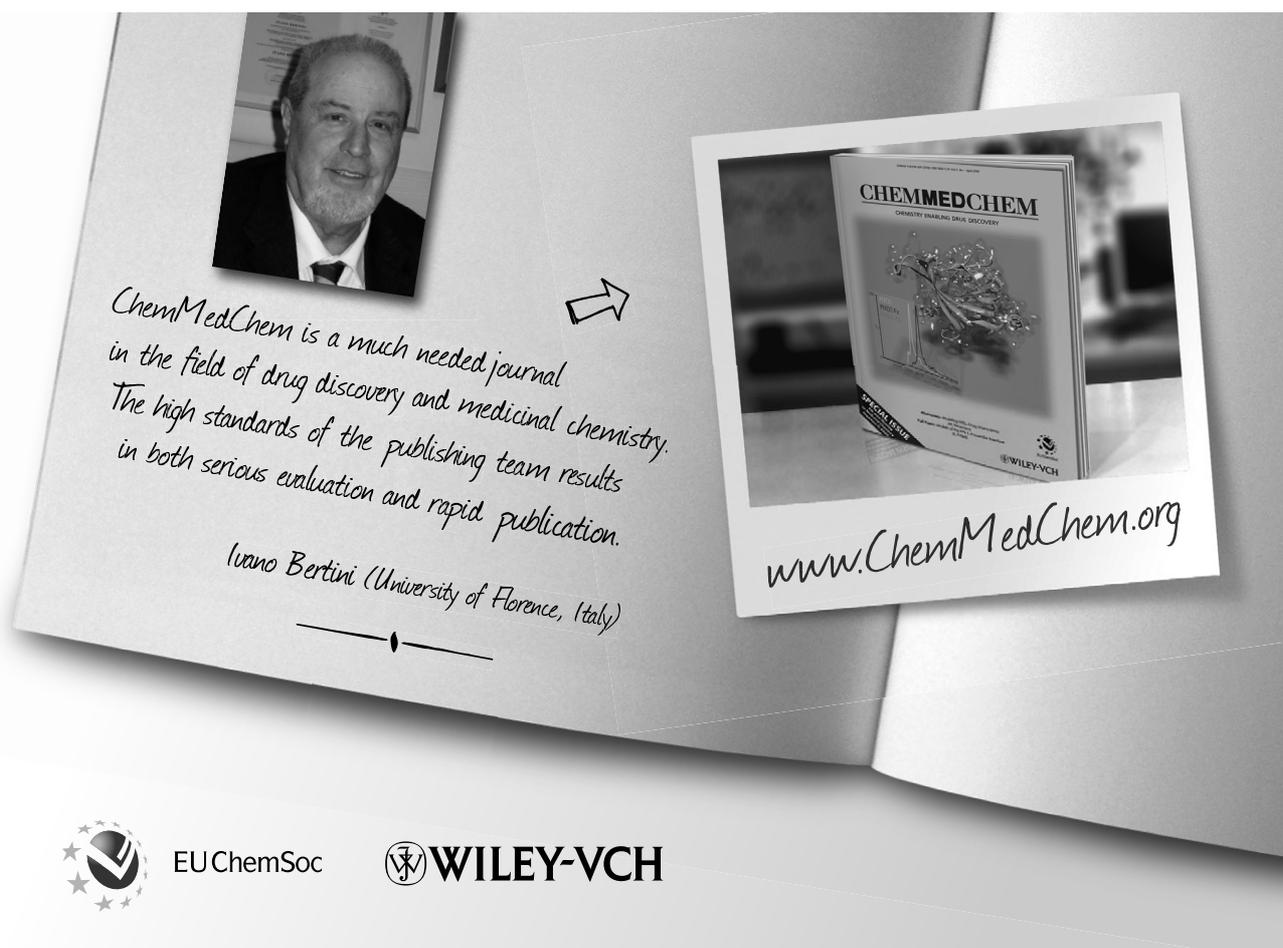
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